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MS APPEAL BRIEF - PATENTS
Docket No.: 1781-0233P
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
GEE, NEOH et al.

Application No.: 09/895,153

Confirmation No.: 9536

Filed: July 2, 2001

Art Unit: 1762

For: PHOTOINDUCED CONVERSION OF
POLYANILINE FROM AN INSULATING
STATE TO A CONDUCTING STATE

Examiner: E. Tsoy

APPEAL BRIEF TRANSMITTAL FORM

MS Appeal Brief - Patents
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Transmitted herewith is an Appeal Brief on behalf of the Appellants in connection with the above-identified application.

The enclosed document is being transmitted via the Certificate of Mailing provisions of 37 C.F.R. § 1.8.

A Notice of Appeal was filed on June 6, 2006.

Applicant claims small entity status in accordance with 37 C.F.R. § 1.27.

The fee has been calculated as shown below:

Extension of time fee pursuant to 37 C.F.R. §§ 1.17 and 1.136(a) - \$@@@.

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Dated: June 6, 2006

Respectfully submitted,

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Attachment(s)



Docket No.: 1781-0233P
(PATENT)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of:
NEOH, et al.

Application No.: 09/895,153

Confirmation No.: 9536

Filed: July 2, 2001

Art Unit: 1762

For: PHOTOINDUCED CONVERSION OF
POLYANILINE FROM AN INSULATING
STATE TO A CONDUCTING STATE

Examiner: Elena TSOY

BRIEF ON APPEAL

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

This is an appeal from the Final Rejection of claim 36.

(i.) Real party in interest.

The real party in interest in this appeal is the Assignee of the involved patent application, National University of Singapore.

(ii.) Related appeals and interferences.

There are no related appeals or interferences.

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(iii.) Status of claims.

Claim 36 stands rejected. Claims 39 and 41-52 are allowed. Claims 1-35, 37, 38, and 40 have been cancelled.

(iv.) Status of Amendments.

No Amendments were filed subsequent to the mailing of the Final Rejection. On March 3, 2006, Applicants filed a Request for Reconsideration, which was accompanied by evidentiary publications. The Examiner considered the Request for Reconsideration, expressing her opinion in an Advisory Action mailed on March 13, 2006.

vi.) Summary of claimed subject matter.

Polyaniline in its insulating (free base) form can be cast into films and coated on substrates. Specification, page 1, lines 13-15. The insulating form of polyaniline can be converted to a conductive form by treatment with aqueous protonic acids or by charge transfer interaction with organic electron acceptors. Specification, page 1, line 15 – page 2, line 24. The degree of electrical conductivity of the converted polyaniline is dependent upon the oxidation state of the polyaniline. Specification, page 2, lines 1-5 and 17-24. The present invention provides electrically conductive polymeric material having resistances decreasing from 10^{10} to $10^5 \Omega/\text{sq}$, irrespective of the oxidation state of the polymeric material. Specification, page 4, lines 2-9. The method for preparing the electrically conductive polymeric material at issue in this appeal includes four sequential steps. One step involves providing a vinyl benzyl halide

grafted film substrate. Specification, e.g. page 11, lines 20-22. One step involves reacting the vinyl benzyl halide grafted film with an equimolar mixture of 4,4' bipyridine and p-xylene dihalide to form a viologen salt-grafted film. Specification, e.g. page 11, lines 22-27. "Viologen" salts are 4,4'-bipyridinium salts. One step involves coating the viologen salt-grafted film with polyaniline to form a polyaniline-coated film. Specification, e.g. page 11, line 27 – page 12, line 2. One step involves exposing the polyaniline-coated film to near-ultraviolet radiation to obtain an electrically conductive polymer. Specification, e.g. page 12, lines 2-5

(vi.) Grounds of rejection to be reviewed on appeal.

The sole issue precluding allowance of the present application is the rejection of claim 36 under 35 U.S.C. § 103(a) as being unpatentable over the combination of JP 56-26977 (Sato), US 4,455,233 (Pohl), US 4,414,080, (Williams), and US 5,016,063 (Beratan).

(viii.) Argument

Applicants submit that the Examiner is improperly using hindsight to assemble individual, unrelated teachings of the references, using the rejected claim as a template. Furthermore, even when combined, the collection of references cited by the Examiner fails to disclose or suggest a significant feature of the invention. Thus, the Examiner has not established a proper case of *prima facie* obviousness of the invention.

In the rejection of record, the references outnumber the sole claim under consideration 4 to 1. While there is no absolute prohibition against references "ganging up" on a claim in this

manner, the chances that a person of ordinary skill in the art would really have been motivated to assemble this motley¹ grouping of references to come up with Applicants' technology *in the absence of Applicants' disclosure* is minimal.

The Final Rejection relies upon the statement of the rejection in the Office Action that was mailed on July 5, 2005. After summarizing the relevant teachings of the Sato reference, the Examiner states:

Sato et al fails to teach that (i) benzyl chloride groups can be grafted on a polymeric substrate other than phenyl-containing substrate using vinyl benzyl chloride instead of $\text{CH}_3\text{OCH}_2\text{Cl}$; (ii) an equimolar mixture of 4,4' bipyridine and p-xylene dihalide is used instead of 4,4' bi pyridyl mono aralkyl halide compound; (iii) instead of polyvinyl alcohol, polyaniline can be used as electron donor for coating the viologen salt layer.

Office Action mailed 07/05/2005, page 3. This summary of major differences between what is claimed herein and what is taught in the closest prior art reference is more reminiscent of an Examiner's Statement of Reasons for Allowance than a rejection. Unfortunately, however, the Examiner here appears to have raked through the patent literature to find individual references that allegedly remedy the deficiencies of the Sato reference.

Sato teaches that his films are homogeneous and slightly yellowish in color. His films develop a bright bluish violet color when irradiated, and then de-color upon heating or standing.

¹ Sato is entitled "Photochromic compositions containing viologen compound blended with solid alcohol" and is assigned to Nippon T & T. Sato relates to photosensitive film technology similar to that of the present invention. Pohl is entitled "Method and apparatus for ion analysis and detection using reverse mode suppression" and is assigned to Dionex Corp. Pohl is concerned with the separation of ions by liquid chromatography. Williams is entitled "Photoelectrochemical electrodes" and is assigned to NASA. Williams relates to photoelectrochemical electrodes. Beratan is entitled "Molecular Implementation of molecular shift register memories" and is also assigned to NASA. Beratan describes a molecular shift register employing an electron transfer mechanism.

POHL IMPROPERLY COMBINED. To remedy one deficiency of the Sato reference, the Examiner cites lines 3-15 in column 8 of Pohl. The cited portion of Pohl teaches grafting vinyl benzyl chloride onto polyethylene tubing “to render it suitable for conversion to ion-exchange form. Thereafter, the grafted tubing is aminated as set forth in [a] U.S. patent application entitled ‘Method And Apparatus For Mobile Phase Ion Chromatography And Membrane Suppression.’” The Examiner fails to indicate why a person of ordinary skill in the photochromic film art would look to the ion exchange chromatography art for ways to change the Sato photochromic technology. Even more significantly, the Examiner fails to indicate why one of ordinary skill in the art would be motivated to “irradiat[e] a polyethylene substrate in a solution of vinyl benzyl chloride instead of chloromethylating polystyrene using $\text{CH}_3\text{OCH}_2\text{Cl}$ ”. Office Action of July 5, 2005, page 4. Simply pointing out that something *could* be done does not make it obvious to do it. “The mere combination of prior art references does not make an invention obvious unless something in the prior art suggests or reasonably implies an *advantage to be derived* from uniting their teachings.” *Creative Pioneer Products Corp. v. K-Mart Corp.*, 5 USPQ2d 1841, 1844 (S.D. Tex 1986) (emphasis supplied).

BERATAN IMPROPERLY CONSTRUED. In their response filed October 13, 2005, in the paragraph bridging pages 8-9 thereof, Applicants explained that:

The Examiner states that Beratan discloses that polyaniline is a suitable electron donor for a viologen salt acceptor. Beratan does not make any conductive material comprising polyaniline. Beratan shows redox cycling between aniline and viologen monomer units in a polymer using a ruthenium bipyridine intermediate. *See*, col. 6, lines 18-22. Such a composition is far afield from one comprising a viologen salt and polyaniline as distinct substances.

Thus, Beratan in fact describes a material that is a co-polymer of aniline and viologen, not an article comprising polyaniline and viologen. Accordingly, the combined references in fact make no suggestion of irradiation of an article comprising polyaniline and viologen to obtain a conductive material. The Examiner has still failed to respond to this point (originally raised in the October 13, 2005 Amendment), either in the Final Rejection or in the Advisory Action.

FAULTY UNDERSTANDING OF MECHANISM. The Examiner has stated that “[P]hotoreduction of a viologen salt by polyaniline occurs by electron transfer when irradiated ...due to electroconductivity...”. Final Rejection, page 5 (emphasis in original). This statement highlights the Examiner’s misunderstanding of the present invention. Electron transfer is the mechanism of an oxidation-reduction reaction. Electron transfer does not imply conduction, *i.e.* movement of electrons through a material under the influence of a voltage gradient.

As evidence of this distinction, Applicants have provided publications by Kamogawa et al., Sampanthar et al., and Ogawa et al. Kamogawa et al. show the exchange of an electron between a viologen molecule and a halide ion. See, e.g. the reaction scheme below Figure 2 on page 1022. The negatively charged halide ion is converted to a neutral halogen atom, and the positively charged tertiary amine of the viologen is also rendered neutral, with the result that the viologen absorption spectrum changes and the viologen becomes colored. This is a classic example of an oxidation-reduction reaction and also of photochromism as described by Sato. Sampanthar et al. show essentially the same reaction in the instance of viologen grafted to a low density polyethylene substrate. Further information of how poly(vinyl alcohol) (PVA) participates in the photoreduction of viologen is seen in Ogawa et al., which describes the change

in color of methyl viologen when it is reduced by absorption of an electron generated by oxidation of PVA by gamma radiation or electron beam radiation (as a model of beta rays). Like the Sato reference, Ogawa et al. do not provide any evidence that any electrical conductivity is achieved. In fact, it is highly unlikely, if not impossible for PVA, a non-conjugated polymer, to allow the transport of electrons along its chains. It is certainly not the case that whenever a substance undergoes oxidation, it becomes electrically conductive. It should be noted that all of Sato, Kamogawa, Sampanthar, and Ogawa suggest that the electrons transferred remain localized. There is no suggestion whatsoever that any material is formed that would provide for electron flow under an imposed voltage gradient, i.e. that a conductive material would be made.

The Examiner argues that it does not matter whether she is right or wrong with respect to whether electron transfer is the same as electroconductivity. She maintains that, regardless of mechanism, the polymeric material of the references would *inherently have the same properties* as the polymeric material produced in the invention of claim 36. It is true that inherency can bar a patent under U.S. law, but this should be inherency in a composition actually disclosed in the prior art, not alleged inherency of a composition that could theoretically be produced by modifying the prior art. The Examiner cites sections 2111.02 and 2112.01 of the Manual of Patent Examining Procedure (MPEP). It is not clear why she cites MPEP 2111.02, which is entitled “Effect of Preamble”. MPEP 2112.01 does discuss inherency, but the context of the discussion indicates that inherency is a consideration where a claim is rejected over a single reference, not over a combination of references.

SUMMARY. Applicants respectfully submit that the cited references fail to establish *prima facie* obviousness of the claimed invention. In particular, there is no teaching or suggestion by the combined references that a conductive polymer can be obtained by irradiation of polyaniline-coated viologen. This feature of the invention is totally lacking from the combined teachings of the references.

For at least the reasons explained above, the combination of Sato JP '977, Pohl '233, Williams et al. '080, and Beratan '063 fail to expressly describe or to suggest the subject matter of claim 36. Accordingly, the rejection of claim 36 under 35 U.S.C. § 103(a) over these references is improper as stated by the Examiner and should be reversed.

If there are any questions concerning the present application, the Examiner is respectfully requested to contact Richard Gallagher (Reg. No. 28,781) at (703) 205-8008.

Dated: June 6, 2006

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(viii.) Claims Appendix:

The sole claim rejected is claim 36:

36. A method for preparing an electrically conductive polymeric material comprising:

- a) providing a vinyl benzyl halide grafted film substrate;
- b) reacting the vinyl benzyl halide grafted film with an equimolar mixture of 4,4' bipyridine and p-xylene dihalide to form a viologen salt-grafted film;
- c) coating the viologen salt-grafted film with polyaniline to form a polyaniline-coated film; and
- d) exposing the polyaniline-coated film to near-ultraviolet radiation to obtain an electrically conductive polymer.

(ix.) Evidence Appendix:

- Ogawa et al., *Radiat. Phys. Chem.*, Vol. 29, No. 5, 353-357 (1987), part of response filed October 13, 2005.
- Kamogawa et al., *Chem. Mater.*, 1991, 3, 1020-1023, part of response filed March 3, 2006.
- Sampanthar et al., *Advanced Materials*, 2000, 12, 1536-1539, part of response filed March 3, 2006.

POLY(VINYL ALCOHOL) FILM CONTAINING METHYL VIOLOGEN AS A HIGHLY SENSITIVE DOSIMETER

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(Received 10 November 1986; in revised form 21 November 1986)

Abstract—Color development of polymer films containing methyl viologen (MV^{2+}) as an electron acceptor by gamma- or electron-beam irradiation was studied. The ionizing radiation induced one-electron reduction of MV^{2+} to produce the intensely blue-colored cation radical (MV^{+*}) in the polymer film. Poly(vinyl alcohol) (PVA) was an excellent matrix for the MV^{+*} formation, leading to the greatest $G(MV^{+*})$ value of 9.8 among the polymers studied. The hydroxy groups of not only polymeric alcohol, PVA, but also monomeric alcohols added to poly(vinyl acetate) film were effective for promotion of the radiolytic one-electron reduction of MV^{2+} . The $G(MV^{+*})$ value obtained by gamma-irradiation of the MV^{2+} -PVA film was enhanced from 9.8 to 12.7 by the addition of sodium formate or potassium formate. The MV^{+*} formed by ionizing radiation in the PVA matrix was extremely stable even when exposed to air. The MV^{2+} -PVA film is useful for a highly sensitive dosimeter in the lower dose range below 10 krad.

INTRODUCTION

Colorless methyl viologen (1,1'-dimethyl-4,4'-bipyridinium dication, MV^{2+}) undergoes one-electron reduction to the intensely blue-colored cation radical (MV^{+*}), as demonstrated in the thermo-, photo-, and electro-chemical reaction systems.⁽¹⁻⁸⁾ Pulse and steady-state radiolysis studies in aqueous solution have also shown the capturing of hydrated electrons by MV^{2+} to produce MV^{+*} .⁽⁹⁻¹²⁾ The blue color of MV^{+*} disappears, due to regeneration of MV^{2+} , immediately when the MV^{+*} is exposed to air in fluid media.^(13,14)

Recently we have studied the photoinduced electron-transfer reaction of methyl viologen salts, especially the dichloride ($MV^{2+}(Cl^-)_2$), in poly(vinyl alcohol) (PVA) film.⁽¹⁵⁾ Both PVA matrix and Cl^- counter ions were shown to act as electron donors to electronically excited MV^{2+} , thus producing stable cation radical MV^{+*} even in the presence of air. The present study has focused on the formation of MV^{+*} in PVA film by exposure to ionizing radiation such as γ -ray and electron beam. We describe herein how the PVA film containing MV^{2+} is applicable to a highly sensitive dosimeter.

EXPERIMENTAL

Methyl viologen dichloride ($MV^{2+}(Cl^-)_2$, >99% pure) was used as received from Aldrich Chemical. Poly(vinyl acetate) (PVAc, low molecular weight), 75% hydrolyzed PVAc (average molecular weight, $M_w = 3.0 \times 10^3$) and poly(vinyl alcohol) (PVA, $M_w = 1.4 \times 10^4$) were supplied by Aldrich Chemical. Hydrolyzed PVAc 87.5% ($M_w = 2.2 \times 10^4$), poly(*N*-

vinyl pyrrolidone) (PVP, $M_w = 3.6 \times 10^5$), and poly(acryl amide) (PAAm, $M_w = 7.1 \times 10^5$) were purchased from Nakarai Chemicals, and poly(acrylic acid) (PAA, 8×10^3 – 1.2×10^4 cps at 30°C) in *ca* 25 wt% aqueous solution from Wako Pure Chemical. All of the polymers were used without purification.

The polymer films containing MV^{2+} , other than PVAc, were prepared by cast-drying of aqueous mixture of the polymers and $MV^{2+}(Cl^-)_2$ on a glass plate for 48 h at room temperature and for another 24 h under reduced pressure of 20 mmHg immediately before irradiation. For preparing an MV^{2+} -PVAc film, methanol was used as solvent instead of water.

Irradiations were performed in N_2 or in air at room temperature with a ^{60}Co γ -ray at a dose rate of 23 krad/h or with 200-kV electron beam at a dose rate of 500 krad/s.

The irradiated films were analyzed at room temperature in air by a Shimadzu UV-200S spectrophotometer.

RESULTS AND DISCUSSION

Characteristics of one-electron reduction of MV^{2+} in PVA film by ionizing radiation

The PVA film containing $MV^{2+}(Cl^-)_2$ showed an absorption maximum at 263 nm due to MV^{2+} , being colorless and transparent.⁽¹⁵⁾ New absorption band maxima at 398 and 605 nm assigned to monomeric cation radical (MV^{+*})^(13,14) appeared by exposure of the PVA film to γ -ray or electron beam, as illustrated typically in Fig. 1. Thus, the ionizing radiation induces one-electron reduction of MV^{2+} to the intensely blue-colored cation radical (MV^{+*}) in the

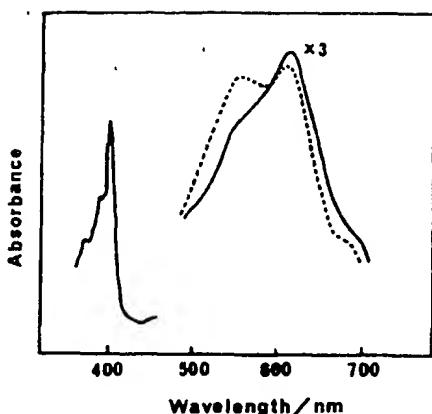


Fig. 1. Representative u.v. spectra of methyl viologen cation radicals: (—) monomeric MV^{2+} ; (---) a mixture of monomeric and dimeric MV^{2+} . The spectra at wavelengths above 500 nm were illustrated with 3-fold magnified absorbance.

PVA film. Another new absorption maximum at 555 nm due to dimeric cation radical ($(MV^{2+})_2$) formation^(15,16) was observed with increasing the radiation dose above *ca* 0.35 Mrad (Fig. 1).

Both monomeric and dimeric MV^{2+} were formed in the PVA film under conditions of higher-dose irradiation. In such a case, the total yield of cation radicals formed in PVA film ($(MV^{2+})_t$) is given by the sum of monomeric (C_m) and dimeric (C_d) terms in mmol/g-PVA unit, as in equation (1).

$$[MV^{2+}]_t = C_m + 2C_d \quad (1)$$

As reported elsewhere,⁽¹⁵⁾ the concentrations of monomeric MV^{2+} and dimeric MV^{2+} can be evaluated spectrometrically by the use of equations (2) and (3),

$$A_{605} = (1014 C_m + 2028 C_d) / l \quad (2)$$

$$A_{555} = (714 C_m + 3028 C_d) / l \quad (3)$$

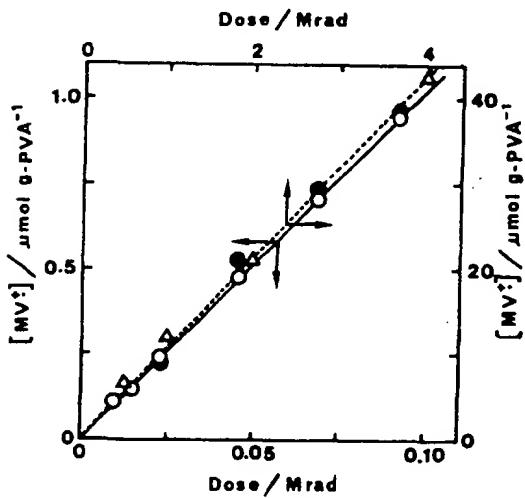


Fig. 2. Dose-yield plots for methyl viologen cation radical (MV^{2+}) formed in poly(vinyl alcohol) film containing methyl viologen (MV^{2+} ; 0.1 mmol/g-PVA) on gamma-irradiation of 780- μ m films (○) in N_2 and (●) in air, and electron-beam irradiation of 40- μ m film (Δ) in N_2 .

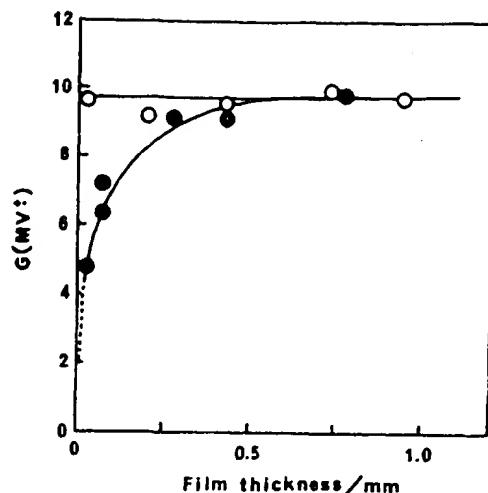


Fig. 3. Dependence of G value of methyl viologen cation radical ($G(MV^{2+})$) on the thickness of poly(vinyl alcohol) film containing methyl viologen (MV^{2+} ; 0.1 mmol/g-PVA): gamma-irradiation (○) in N_2 and (●) in air.

where A_{605} and A_{555} are the absorbances at 605 and 555 nm, respectively, and l is the film thickness in mm unit.

The total yield of cation radicals, $(MV^{2+})_t$, calculated for the gamma-irradiated PVA film (780 μ m thick) following the above procedure increased linearly with increasing the radiation dose (D), independent of the irradiation atmosphere whether in N_2 or in air (Fig. 2). From the slope of this linear plot, the G value for the MV^{2+} formation ($G(MV^{2+})$) was obtained as 9.8 ± 0.6 . Figure 3 shows variation of the $G(MV^{2+})$ values as a function of the MV^{2+} -PVA film thickness. In the case of gamma-irradiation in N_2 , the $G(MV^{2+})$ value was almost independent of the film thickness. On the other hand, the $G(MV^{2+})$ value in air decreased with decreasing the film thickness from 300 μ m, although it was little affected in the greater range of thickness from 300 to 1000 μ m. As discussed below, the behavior in air is attributable to partial quenching of MV^{2+} by O_2 (see also equation (15)) occurring in the near-surface region of the irradiated MV^{2+} -PVA film. It is also noted that the optimum initial concentration of $MV^{2+}(Cl^-)_2$ for obtaining higher $G(MV^{2+})$ value ranged from 0.05 to 0.1 mmol/g-PVA. Thus, under the present conditions the ultimate $G(MV^{2+})$ value was 9.8 using the MV^{2+} -PVA film.

For comparison, the MV^{2+} -PVA film (40 μ m thick) was exposed to 200-kV electron beam in N_2 . The depth-dose curve, which was measured for the 200-kV electrons with a plastic dosimeter of cellulose triacetate film, showed the maximum dose at *ca* 40 μ m depth. It is also indicated that the dose is almost constant (98–100% in relative value) for the MV^{2+} -PVA films with thickness below 100 μ m. As shown in Fig. 2, the dose-response of $(MV^{2+})_t$ on the electron-beam irradiation was practically equivalent to the gamma-irradiation of 780- μ m film; $G(MV^{2+})$

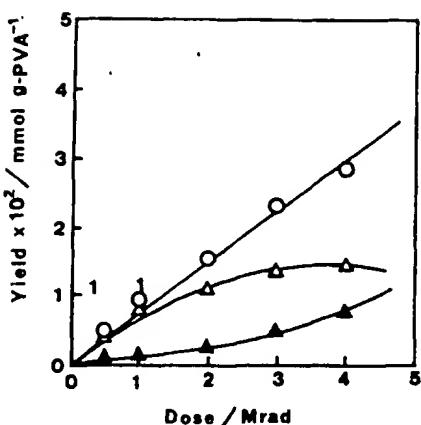
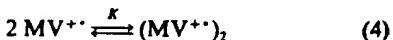


Fig. 4. Dose-yield plots of (○) total methyl viologen cation radical ($(MV^{•+})_t = C_m + 2C_d$), (△) monomeric $MV^{•+}$ (C_m), and (▲) dimeric $MV^{•+}$ (C_d) on gamma-irradiation of poly(vinyl alcohol) film (70 μ m thick) containing methyl viologen (MV^{2+} ; 0.1 mmol/g-PVA) in air.

value was obtained as 10.4 ± 0.9 . Similarly, the electron-beam irradiation of 100- μ m film resulted in nearly equal $G(MV^{•+})$ value of 9.2.

In contrast to $(MV^{•+})_t$, the plots of C_m and C_d vs D gave upward-convex and concave curves, respectively (Fig. 4). The formation of dimeric $MV^{•+}$ was negligibly small at radiation doses lower than ca 0.35 Mrad, while it was favored by the increasing total yield of cation radicals, $[MV^{•+}]$. These results show that the dimeric $MV^{•+}$ is attributed to the enhanced association of monomeric $MV^{•+}$, as in equation (4).^(16,17)



The apparent association constant $K (= C_d / C_m^2)$ in the PVA film was evaluated as 34 g-PVA/mmol from the linear portion of Fig. 5. This K value (equivalent to $34 M^{-1}$ on assuming the density of PVA as 1 g/cm³) in the solid PVA matrix is one order of magni-

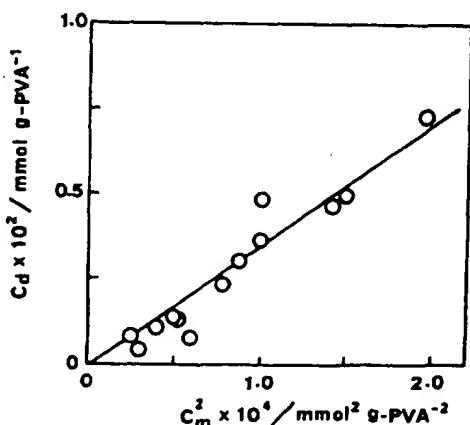


Fig. 5. Linear relationship between dimeric and monomeric methyl viologen cation radicals ($MV^{•+}$), C_d vs C_m^2 , formed on gamma-irradiation of poly(vinyl alcohol) film containing methyl viologen (MV^{2+} ; 0.1 mmol/g-PVA).

tude smaller than the reported value ($ca 400 M^{-1}$)⁽¹⁶⁾ in solution. It is reasonable to expect that the association of monomeric $MV^{•+}$ in the solid is significantly depressed due to the restricted mobility.

Effect of various polymer matrices on the radiolytic reduction of MV^{2+}

In order to clarify what type of polymer is the best matrix for the $MV^{•+}$ formation by gamma-irradiation, we further evaluated the $G(MV^{•+})$ values in poly(vinyl acetate) (PVAc), poly(acrylic acid) (PAA), and poly(*N*-vinyl pyrrolidone) (PVP) films.

As listed in Table 1, the $MV^{•+}$ formation could not be observed upon exposing MV^{2+} -PVAc film to γ -rays in N_2 . The $G(MV^{•+})$ value became greater with increasing the saponification value of PVAc, thus increasing the amounts of hydroxy groups of polymer matrix. The maximum $G(MV^{•+})$ value of 9.8 ± 0.6 was achieved using PVA (i.e. 100% hydrolyzed PVAc) matrix. These results suggest that the hydroxy groups of PVA play an important role in the radiolytic reduction of MV^{2+} to $MV^{•+}$.

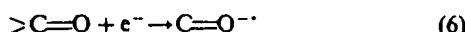
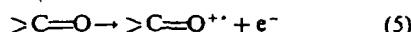
The $G(MV^{•+})$ values in PAA and PVP films were 0.3 and 4.6, respectively, and were smaller than in PVA film. Because of the failure to prepare a good film of poly(acryl amide) (PAAm) containing $MV^{•+}(Cl^-)_2$, we made a comparative experiment using a mixed polymer film of PAAm and PVA (1:1 weight ratio) (see Table 1). The $G(MV^{•+})$ value in the PAAm/PVA mixed film was 2.2, which was much smaller than in one-component PVA film. It is thus suggested that PAAm is a much less effective matrix for the radiolytic $MV^{•+}$ formation. Among the polymers studied, except for PVA, PVP gave the greatest $G(MV^{•+})$ value, probably due to an N atom in the side-chain pyrrolidone group acting as a strong electron donor to MV^{2+} . It is apparent that the side-chain groups of the vinyl polymers play a crucial role as electron donors in the radiolytic reduction of MV^{2+} to $MV^{•+}$. PVA is the best polymer matrix for $MV^{•+}$ formation. All the polymers such as PVP, PAA, PVAc and PAAm, which have electron accepting carbonyl ($>C=O$) groups in their side chains, decreased the $G(MV^{•+})$ value relative to PVA. It seems likely that the net electron-transfer ability of the side-chain $>C=O$ groups of these polymers toward MV^{2+} are much smaller than that of the hydroxy groups of PVA, as a result of either back

Table 1. G values of methyl viologen cation radical ($G(MV^{•+})$) formed in various polymer films containing methyl viologen (MV^{2+}) on gamma-irradiation in N_2

Polymer film		$G(MV^{•+})$
Poly(vinyl acetate)	PVAc	0
75.0% Hydrolyzed PVAc		4.5 ± 0.2
87.5% Hydrolyzed PVAc		5.7 ± 0.4
Poly(vinyl alcohol)	PVA	9.8 ± 0.6
Poly(acrylic acid)	PAA	0.3 ± 0.1
Poly(<i>N</i> -vinyl pyrrolidone)	PVP	4.6 ± 0.1
PVA-Poly(acryl amide)	PVA-PAAm	2.2 ± 0.1

^a $(MV^{2+}) = 0.1 \text{ mmol/g-polymer}$; polymer films were 780 μm thick.

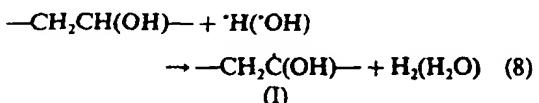
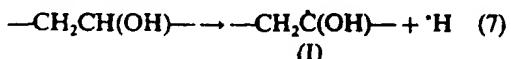
electron-transfer reaction (equation (5)) or electron-capture reaction [equation (6)].⁽¹⁹⁾



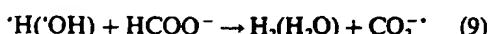
Effect of additives on the radiolytic reduction of MV²⁺ in polymer matrix

Addition of ethylene glycol to the nonsensitive PVAc film containing MV²⁺ gave rise to absorption at 605 nm due to MV⁺ upon gamma-irradiation, while the effect of ethers was negligibly small (Table 2). This observation indicates that the hydroxy groups of not only polymeric alcohol, PVA, but also monomeric alcohols added to the inert PVAc matrix are effective for the radiolytic one-electron reduction of MV²⁺ to MV⁺.

It is known that the radiolysis of alcohols generates several kinds of reducing species such as solvated electrons (e_{sol}^-), hydrogen atoms ($\cdot\text{H}$) and alcohol-derived radicals ($\text{R}_1\text{R}_2\dot{\text{C}}(\text{OH})$).⁽²⁰⁻²²⁾ Either e_{sol}^- or $\text{R}_1\text{R}_2\dot{\text{C}}(\text{OH})$ is main species for the reduction of MV²⁺.^(9,12) The formation of similar radicals, $-\text{CH}_2\dot{\text{C}}(\text{OH})-$, in the gamma-irradiated solid PVA has also been observed at room temperature by ESR measurement.⁽²³⁻²⁵⁾ In the present study, the G value for MV⁺ formation in PVA film by gamma-irradiation was enhanced from 9.8 to 12.7, when sodium formate or potassium formate was added (Table 3). The role of the formate seems to be an efficient conversion of radicals to a reducing species of CO_2^- , which is reactive toward MV²⁺.^(11,26) The increment of $G(\text{MV}^+)$ in PVA film with excess amounts of formate was 2.9, which is comparable to the concentration of PVA-derived radicals ($G = 2.5$) determined by ESR at room temperature. Thus, the promotion effect of formate on the MV⁺ formation may be related to the formation of PVA radicals (I), as in equations (7) and (8).^(27,28)



Reaction (9) may also occur in the presence of formate.



It is likely that the enhanced $G(\text{MV}^+)$ value (the

Table 2. Effect of additives on radiolytic formation of methyl viologen cation radical (MV⁺) in poly(vinyl acetate) film^a

Additive	Absorbance at 605 nm
None	0
Ethylene glycol	0.21
Ethylene glycol monooethyl ether	0.03
Ethylene glycol diethyl ether	<0.01

^a(MV²⁺) = 0.1 mmol/g-PVAc; (additive) = 10 mmol/g-PVAc; radiation dose = 1.15 Mrad.

Table 3. Promotion effect of formates on radiolytic formation of methyl viologen cation radical (MV⁺) in poly(vinyl alcohol) film^a

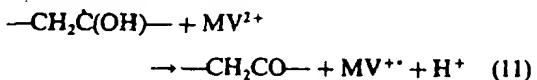
Formate	$G(\text{MV}^+)$
None	9.8 ± 0.6
Sodium formate	12.8 ± 0.6
Potassium formate	12.6 ± 0.1

^a(MV²⁺) = 0.1 mmol/g-PVA; (formate) = 1.0 mmol/g-PVA; PVA films were 780 μm thick.

increment of 2.9) in PVA film with formate is mainly due to the reduction of MV²⁺ by CO_2^- , as in equation (10).



It is known that $\text{R}_1\text{R}_2\dot{\text{C}}(\text{OH})$ radical has ability for one-electron reducing MV²⁺.^(9,12) The corresponding PVA-derived radical may also be reactive toward MV²⁺, as in equation (11).

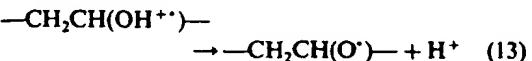


The $G(\text{MV}^+)$ value due to reaction (11) is presumed to be smaller than the G value (= 2.5) for the $-\text{CH}_2\dot{\text{C}}(\text{OH})-$ radicals at room temperature.

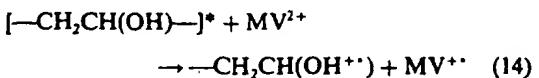
In view of the greater $G(\text{MV}^+)$ value of 9.8 in PVA film, the radiolytic electron ejection (equation (12)) would be an important process for the reduction of MV²⁺ to MV⁺.



The polymer cation radical thus produced is probably converted to the following type of polymer radical that may reduce MV²⁺.^(3,29)



In addition, electronically excited PVA would account for the enhanced formation of MV⁺ in PVA film.



Utility of MV⁺-PVA film in dosimetry

The linear relationship between $(\text{MV}^+)_t$ and radiation dose, as in Fig. 4, shows that the MV²⁺-PVA film is applicable to a dosimeter. Particularly, the MV²⁺-PVA film is useful for the determination of lower doses of γ -ray below 10 krad, because both the absorbances at 398 and 605 nm due to monomeric MV⁺ increased linearly with dose in its lower range; thus, the formation of dimeric cation radical (MV⁺)₂ is negligible. In this case, higher sensitivity may be obtained using the absorption of MV⁺ at 398 nm because of the higher extinction coefficient. Several types of commercially available film dosimeters are commonly used for the determination of absorbed doses above 0.5 Mrad.^(30,31) In the comparative experiments, the sensitivity of the MV²⁺-PVA film

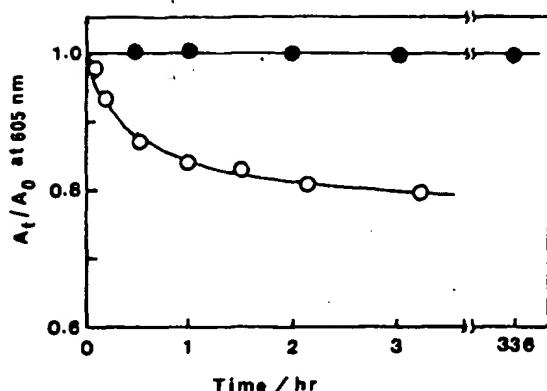
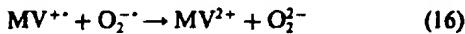
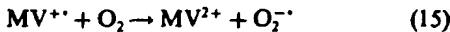


Fig. 6. Decay of methyl viologen cation radical ($MV^{+}\cdot$) in poly(vinyl alcohol) films (○) without and (●) with polypropylene-poly(vinyl alcohol) laminate pack: A_0 , absorbance immediately after gamma-irradiation; A_t , absorbance at a given time after gamma-irradiation and exposure to air.

to γ -ray was ca 2500-fold greater than those of the commercially available dosimeters.

For practical use as a dosimeter, the stability of $MV^{+}\cdot$ in PVA film should be one of the important demands. In the previous study,⁽¹⁵⁾ fading of the characteristic blue color of $MV^{+}\cdot$ produced photochemically in the PVA matrix was observed when exposed to air. This behavior was interpreted in terms of one-electron oxidation of the $MV^{+}\cdot$ by O_2 to regenerate colorless MV^{2+} (equations (15) and (16)).



This fading was promoted when the PVA film was humidified, probably due to the enhanced oxygen permeability with increased water content.⁽¹⁵⁾

Figure 6 shows the time decay in air of $MV^{+}\cdot$ formed in the gamma-irradiated PVA film. The decrease in the absorbance at 605 nm due to monomeric $MV^{+}\cdot$ was extremely slow, in contrast to prompt decreases in aqueous and alcoholic solutions upon exposure to air. Thus, the $MV^{+}\cdot$ formed in solid PVA matrix is unusually stable even in air.

In order to gain further stability of $MV^{+}\cdot$ in PVA film, the MV^{2+} -PVA film was packed in *vacuo* with thin laminate film composed of PVA and poly(propylene), before irradiation. The outer jacketed film could protect the $MV^{+}\cdot$ formed in the inner PVA film from air and water; the $MV^{+}\cdot$ was stable for at least 2 weeks in the presence of air, as shown in Fig. 6. In addition, using the vacuum-packed film, no decrease in the absorbance at 605 nm of monomeric $MV^{+}\cdot$ was observed for several hours even in water.

Further characterization of the $MV^{+}\cdot$ -PVA film for its application to dosimetry will be reported in a subsequent paper.

CONCLUSIONS

The present study has shown that MV^{2+} is subject to one-electron reduction to produce the intensely blue-colored $MV^{+}\cdot$ in solid PVA matrix by ionizing radiation such as γ -ray and electron beam. The $MV^{+}\cdot$ -PVA film is useful as a dosimeter for radiation doses lower than 10 krad.

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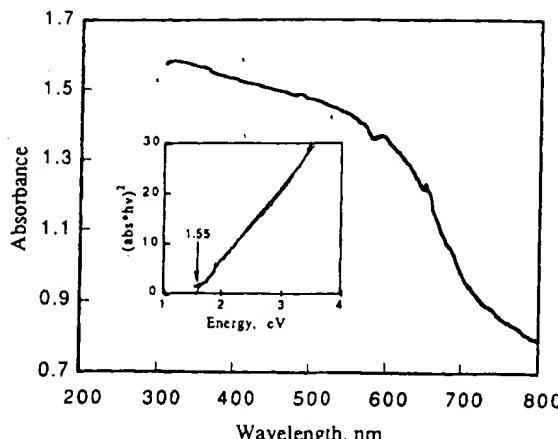


Figure 9. Absorption spectrum of CdSe film as deposited on Ti and removed with Scotch tape. The inset shows a plot of $(\text{absorbance} \times h\nu)^2$ vs $h\nu$ for the same sample.

band edge was not as obvious in all films analyzed, indicating that the electronic properties of this material vary somewhat from sample to sample. Presumably this arises from the very fine grain structure in these films. Deviations from the expected bulk properties of CdSe films have previously been attributed to quantum confinement effects arising from the very small crystallite size obtained with electrodeposited films.^{14,17,18} Hot-probe measurement of the as-deposited CdSe films indicated that the material in n-type.

Conclusions

The cyclic electrodeposition technique used in the present study produces homogeneous films of CdSe that

are close to 1:1 atomic ratio of Cd to Se. The scan parameters are designed to lay down sequential monolayers of CdSe in order to avoid the accumulation of excess Se in the material. For the purpose of producing stoichiometric semiconductor films, this is an improvement over previous potentiostatic or galvanostatic electrochemical techniques, which tend to produce films containing excess Se. The key feature in this process appears to be the continuous deposition and stripping of excess Cd, which is proposed to react with any excess Se that may deposit. The material produced by sequential monolayer electrodeposition contains 3-4% by weight Cl as the major impurity when CdCl_2 is used as the Cd source. The films produced using the present technique consist of a dense layer underneath scattered dendrites, similar to CdSe films electrodeposited by other routes. In addition, the optical properties of these films are similar to those of previously studied films. Thus, although the present technique provides an improvement in the stoichiometry of electrodeposited films, in other respects the films do not significantly differ from those made by previous routes. Current work is directed at elucidating the mechanism of CdSe growth, characterizing the electronic properties of these films, and extending the procedure to other semiconductor systems.

Acknowledgment. We thank Jan Talbot for helpful discussions. A.M.K. thanks the U.S. Department of Education for a graduate fellowship.

Registry No. CdSe, 1306-24-7; Ti, 7440-32-6; Ni, 7440-02-0; CdCl_2 , 10108-64-2; CdSO_4 , 10124-36-4; SeO_2 , 7446-08-4; H_2SeO_3 , 7783-00-8.

Redox Photochromism in Films of Viologens and Related Compounds Bearing Long-Chain Alkyl Groups

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1,1'-Bis(benzyl or *p*-methylbenzyl)-4,4'-bipyridinium and *trans*-4,4'-vinylenebis(1-benzylpyridinium) bis(*p*-alkylbenzenesulfonate)s bearing long-chain alkyl groups (viologen Ia,b), prepared from their respective dichlorides by the anion-exchange reaction, were sandwiched between two glass plates by melting to afford thin transparent and mainly isotropic films. These almost colorless or pale yellow films developed intense visible colors by near-UV irradiation, which bleached upon heating (photochromism). This behavior is considered to be due to reversible redox reactions consisting of the one-electron transfer to viologen Ia,b dication from the counteranion by the photon mode (color development) and vice versa by the heat mode (bleaching).

Introduction

It has been widely known that some 1,1'-disubstituted bipyridinium, i.e., viologens, and related salts reversibly develop intense colors with visible lifetimes when exposed to radiation of the solar level in solutions in the presence of reductants,¹ in activating matrix polymer films,² and in

the crystalline state.³

We report here reversible photoreductions accompanied by visible color developments (photochromism), which have been found for thin isotropic films made of the viologens bearing long-chain alkyl groups without any

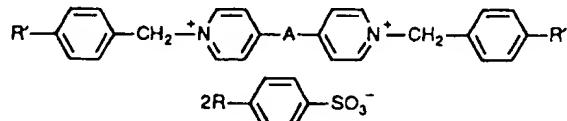
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additives. This has made possible for the first time the color development by light of transparent films based on a redox mechanism consisting of the photon mode color development and the heat mode bleaching.

The compounds prepared and investigated in this study, which are hereafter referred to as "viologens", are shown in Ia,b, where R represents alkyl groups with C_6-C_{15} .



Ia,b: A = none (Ia) or $-CH=CH-$ (Ib); R' = H or CH_3

Experimental Section

Materials. All reagents employed were of the highest purity and used as received, unless otherwise noted. The alkyl groups (R) of *p*-alkylbenzenes were identified by means of mass spectrometry and gas chromatography.

Instrumentation. Infrared (IR), ¹NMR, mass, and EPR spectra were recorded on a Hitachi 215 spectrophotometer, a JNM-PMX 60 spectrometer, a Hitachi M808MS spectrometer, and a JES-FE1 XG spectrometer, respectively, under standard conditions. Elemental analyses were made with a Perkin-Elmer 240 instrument. Visible absorption spectra were obtained with a Shimazu UV-160 spectrophotometer. Gas chromatography was carried out with a Hitachi 164 gas chromatograph fitted with a SE-30 column under a helium stream (30 mL min⁻¹).

1,1'-Dibenzyl-4,4'-bipyridinium Bis(*p*-alkylbenzenesulfonate) (Ia, R' = H). 1,1'-Dibenzyl-4,4'-bipyridinium dichloride (0.10 g, 0.24 mmol), prepared by refluxing 4,4'-bipyridine with benzyl chloride for 24 h, was dissolved in hot ethanol (50 mL). To the resulting solution was added an anion-exchange resin (Amberlite IRA-900, capacity, 1 mg equiv/mL; 10 mL), loaded with *p*-alkylbenzenesulfonate anion by exchanging the OH⁻ type with *p*-alkylbenzenesulfonic acid, which had been synthesized by the sulfonation of *p*-alkylbenzene with 30% fuming sulfuric acid, followed by stirring at 30 °C overnight. The resin was filtered off, and the filtrate was concentrated on a rotary evaporator and precipitated into ether (200 mL) to provide crude product, which was purified by recrystallization from ethanol-ether.

Anal. Calcd for $C_{48}H_{68}N_2S_2O_6$ (R = *n*-C₆H₁₃): C, 70.24; H, 6.83; N, 3.41%. Found: C, 70.12; H, 6.90; N, 3.31%. Calcd for $C_{62}H_{76}N_2S_2O_6$ (R = *n*-C₉H₁₇): C, 71.24; H, 7.76; N, 3.19%. Found: C, 71.25; H, 7.83; N, 3.22%. Calcd for $C_{54}H_{68}N_2S_2O_6$ (R = *n*-C₉H₁₉): C, 71.69; H, 7.52; N, 3.10%. Found: C, 71.60; H, 7.48; N, 3.09%. Calcd for $C_{56}H_{72}N_2S_2O_6$ (R = *n*-C₁₀H₂₁): C, 72.11; H, 7.72; N, 3.00%. Found: C, 72.48; H, 7.75; N, 2.86%. Calcd for $C_{58}H_{76}N_2S_2O_6$ (R = *n*-C₁₁H₂₃): C, 72.50; H, 7.92; N, 2.92%. Found: C, 72.64; H, 7.97; N, 2.90%. Calcd for $C_{60}H_{80}N_2S_2O_6$ (R = *n*-C₁₂H₂₅): C, 72.87; H, 8.10; N, 2.83%. Found: (R = *n*-C₁₂H₂₅): C, 72.58; H, 8.13; N, 2.90%. (Film no. 11 in Table III): C, 72.84; H, 8.14; N, 2.88%. Calcd for $C_{62}H_{84}N_2S_2O_6$ (R = *n*-C₁₃H₂₇): C, 73.23; H, 8.27; N, 2.76%. Found: C, 73.20; H, 8.23; N, 2.76%. Calcd for $C_{64}H_{88}N_2S_2O_6$ (R = *n*-C₁₄H₂₉): C, 73.57; H, 8.42; N, 2.68%. Found: C, 73.30; H, 8.37; N, 2.66%. Calcd for $C_{66}H_{92}N_2S_2O_6$ (R = *n*-C₁₅H₃₁): C, 73.88; H, 8.58; N, 2.61%. Found: C, 73.45; H, 8.51; N, 2.63%.

IR (KBr) 1190, 1030 (SO₃⁻) cm⁻¹. ¹H NMR (DMSO-d₆) δ 0.5–2.0 (m, alkyl), 2.5 (t, 4 H, 2CH₂), 6.0 (s, 4 H, 2CH₂), 6.9–8.0 (m, 18 H, ArH), 8.8 (d, 4 H, pyridinium), 9.4 (d, 4 H, pyridinium).

1,1'-Bis(*p*-methylbenzyl)-4,4'-bipyridinium Bis(*p*-decylbenzenesulfonate) (Ia, Film No. 12 in Table III). The same reaction procedure as that for Ia (R' = H) was applied to 1,1'-bis(*p*-methylbenzyl)-4,4'-bipyridinium dichloride to provide a colorless crystalline powder. **Anal.** Calcd for $C_{62}H_{84}N_2S_2O_6$: C, 73.23; H, 8.27; N, 2.76%. Found: C, 73.17; H, 8.30; N, 2.66%. IR (KBr) 1200, 1040 (SO₃⁻) cm⁻¹. ¹H NMR (DMSO-d₆) δ 0.5–2.0 (m, 46 H, 2C₁₁H₂₃), 2.3 (s, 6 H, 2CH₃), 2.5 (t, 4 H, 2CH₂), 5.9 (4 H, 2CH₂), 6.9–7.8 (m, 16 H, ArH), 8.8 (d, 4 H, pyridinium), 9.5 (d, 4 H, pyridinium).

trans-4,4'-Vinylenebis(1-benzylpyridinium) Bis(*p*-decylbenzenesulfonate) (Ib, Film No. 13 in Table III). This colorless compound was synthesized in the same manner as for

Ia (R' = H), starting with *trans*-4,4'-vinylenebis(1-benzylpyridinium) dichloride, also prepared using *trans*-1,2-bis(4-pyridyl)ethylene instead of 4,4'-bipyridine. **Anal.** Calcd for $C_{62}H_{82}N_2S_2O_6$: C, 73.37; H, 8.09; N, 2.76%. Found: C, 73.25; H, 8.12; N, 2.71%. IR (KBr) 1180, 1040 (SO₃⁻) cm⁻¹. ¹H NMR (DMSO-d₆) δ 0.5–0.2 (m, 46 H, 2C₁₁H₂₃), 2.5 (t, 4 H, 2CH₂), 5.9 (s, 4 H, 2CH₂), 7.0–7.9 (m, 18 H, ArH), 8.2 (s, 2 H, —CH=CH—), 8.5 (d, 4 H, pyridinium), 9.3 (d, 4 H, pyridinium).

Preparation of the Glass-Sandwiched Film. Finely divided crystals of viologen Ia,b were spread on a glass plate and melted quickly (above 140 °C), followed by the immediate tight covering with another glass plate and cooling to room temperature to afford an almost air-tight glass-sandwiched film ranging in thickness from 0.008 to 0.012 mm. All these operations were carried out in a glovebox filled with purified nitrogen.

The film thus prepared was transparent and almost colorless or pale yellow. The isotropic property of the film was checked with crossed polarizers.

Light Sources for Photochromic Measurements. The glass-sandwiched films were subjected to the 10-min irradiation by 366-nm UV light, obtained by passing the light from a 75-W high-pressure mercury lamp (Toshiba SHL-100UV) through a JASCO CT-10S monochromator. A 150-W xenon lamp, fitted with a Toshiba O-59 filter cutting the light below 590 nm, was employed for the visible irradiation on the film, which had been irradiated with the near-UV light and had developed color.

Since the viologens and related compounds described above belong to the same compound group as a herbicide Paraquat,⁴ handling in an appropriate manner so as to avoid exposure is recommended.

Results and Discussion

Viologens Ia,b were synthesized starting with 1,1'-bis(benzyl or *p*-methylbenzyl)-4,4'-bipyridinium dichloride or *trans*-4,4'-vinylenebis(1-benzylpyridinium) dichloride by the anion-exchange reaction using an anion-exchange resin.

Fine powders of the viologens thus synthesized were heated just to their melting points (>140 °C) under nitrogen and then sandwiched between two glass plates to provide air-tight thin films free of oxygen. The glass-sandwiched films thus prepared, which were transparent and mainly isotropic, were subjected to near-UV irradiation (366 nm) from a 75-W high-pressure mercury lamp for 10 min, and the resulting absorbance increases in the visible region were recorded.

With the irradiation, initially colorless or pale yellow films gradually developed visible colors with almost linear increases of absorbances.

Figure 1 indicates typical absorption spectra obtained when the irradiation was stopped after 10 min.

It is recognized in this figure that absorption spectra based on the transmission of light, the measurements of which had been impossible for viologen crystals,³ could be determined satisfactorily.

The shape and position of absorption maximum (ca. 600 nm, blue coloration) of curve 1 are quite similar to those of the radical cations derived from the conventional viologens in solutions⁵ and viologen crystals,³ and those of curve 2 are also consistent with the characteristics of the absorption spectra including a lot of the associated radical cations.⁶ Moreover, EPR spectra exemplified in Figure 2 correspond exactly to the absorption change, so that it is confirmed that the radical cation was produced by the one-electron transfer from the counteranion to viologen dication, as demonstrated in the case of viologen crystals.³ However, no appreciable differences in the IR

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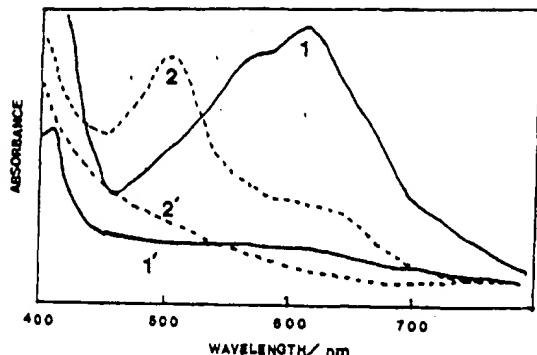


Figure 1. Typical visible absorption spectra for the glass-sandwiched viologen Ia,b films subjected to near-UV irradiation. Curves 1 and 1' indicate the spectrum immediately after irradiation and that before irradiation or upon a 10 min standing at 70 °C after irradiation, respectively, in the case of $R = 70\% n + 30\% \text{ highly branched } C_{12}\text{H}_{25}$ and $R' = H$ (Ia); curves 2 and 2' are those in $R = n\text{-C}_4\text{H}_{29}$. The measure of absorbance is arbitrary only to show the shapes of absorption spectra.

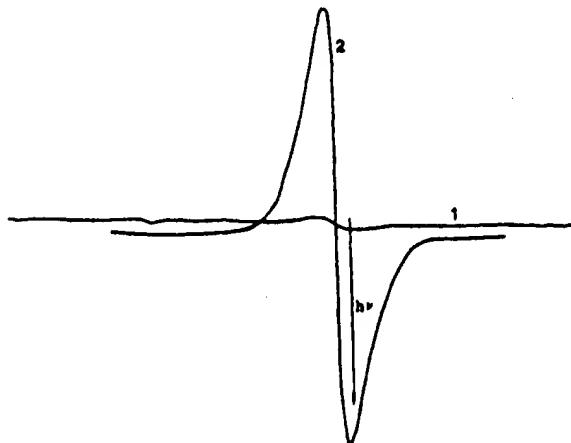
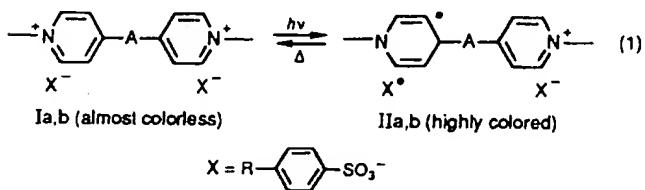


Figure 2. Typical EPR spectra for the glass-sandwiched viologen Ia,b films subjected to near-UV irradiation. Spectra 1 and 2 correspond to 1' and 1 in Figure 1, respectively. Measurement conditions: field, 3290 G + 250 G; modulation 100 kHz; amplitude, 1.25×10^{-3} ; response, 0.01.

spectrum were recognized between before and after irradiation, presumably because the change in concentration is so small as to not be detectable.

Figure 1 also indicates that these increases in visible absorption induced by light can be recovered to the original states 1' and 2' upon 10 min of standing at 70 °C.

Such being the case, the reversible relation given in eq 1 may exist between the original viologen Ia b and the



radical ion pair IIa,b produced as a result of irradiation. Namely, as for viologens Ia,b bearing long alkyl chains, reversible photoredox reactions, i.e., intense color development by the photon mode and bleaching of the developed color by the heat mode (redox photochromism), may take place in the absence of oxygen.

A typical example indicating the effect of temperature on bleaching of the color developed by light is given in Table I. It is recognized in this table that the initial bleaching rate (A/A_0) at λ_{\max} increased rapidly with temperature, and in this case bleaching was almost complete

Table I. Effect of Temperature on Bleaching of the Color Developed in a Typical Viologen Film^c by Near-UV Light

expt. no.	temp, °C	init bleaching rate ^b A/A_0 (613 nm), min ⁻¹
1	30	0.03
2	40	0.24
3	50	0.66
4	60	0.72
5	70	0.99
6	80	1.00
7	90	1.48
8	70	2.10 ^c
9	70	0.12 ^d
10	Xe lamp ^e	0.01

^a Viologen corresponding to curves 1 and 1' in Figure 1 [$R = 70\% n + 30\% \text{ highly branched } C_{12}H_{26}$; $R' = H$ (Ia)]. ^b A_0 : absorbance increase at 613.0 nm induced by light. A: Initial decrease of absorbance reduced to 1 min. ^c In the presence of a half-molar excess of *p*-dodecylbenzenesulfonic acid. ^d Viologen anions are composed of $RPhSO_3^- - Cl^-$ in 3:1 molar ratio. ^e 150 W, >590 nm, 5 cm \times 1 h.

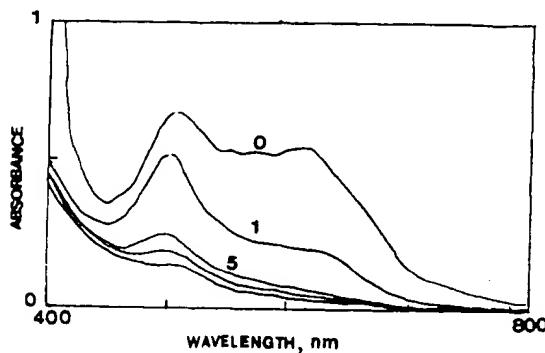


Figure 3. Typical change of the visible absorption spectra developed for viologen Ia,b films by light with heating at 70 °C. Absorption spectra are those for viologen Ia with R = 70% *n*- + 30% highly branched C₁₂H₂₅ and R' = CH₃. Figures in the diagram denote standing times at 70 °C in minutes after irradiation.

at 70 °C in 1 min (expt no. 5). Irradiation of visible light above 590 nm on the colored film, however, provided little changes (expt no. 10), thereby suggesting that the back reaction was of the heat mode nature. It can be also seen in Table I that the presence of excess *p*-dodecylbenzenesulfonic acid in the film enhanced the bleaching rate significantly (expt no. 8), presumably due at least partly to a plasticizing effect; lack of $RPhSO_3^-$ caused the reverse effect (expt no. 9), as expected.

It is also recognized in Figure 3 that the absorbance peak around 600 nm attributable to the monomeric radical cation, as mentioned above, decreases more rapidly by heating than the peak around 500 nm attributable to the associated ones does, indicating that the former is less stable thermally than the latter. This is a general tendency in the present study.

Effects of the kind of viologen Ia,b on the visible absorption changes induced by light, i.e., photochromic behavior by redox mechanism, as determined by transmittance, are summarized in Tables II and III.

It is known from Table II that both isotropic properties and photoredox behavior of the film are affected significantly by the chain length of R. Thus, as for Ia with R composed of an *n*-alkyl group alone, the values of the absorbance increase induced by UV irradiation were reduced to those for the 0.01-mm film thickness in order to prevent errors caused by slight deviations from 0.01-mm thickness. The corrected absorbance increase, i.e., photosensitivity, at λ_{max} around 500 nm appears to first become larger with an increase in carbon number to reach

Table II. Effect of Chain Length of R on Photochromic Behavior of Vologen Ia (R' = H) Films^a

film no.	R	abs increase ^b induced by light		A/A ₀ , ^c min ⁻¹	isotropic ^d property of film
		ca. 500 nm	610 nm		
1	n-C ₆ H ₁₃	0.362 (504) ^e	0.190	0.36	transparent but a little anisotropic
2	n-C ₈ H ₁₇	0.625 (505) ^e	0.318	0.45	transparent but a little anisotropic
3	n-C ₉ H ₁₉	0.788 (506) ^e	0.421	0.48	transparent and isotropic
4	n-C ₁₀ H ₂₁	0.787 (506) ^e	0.451	0.52	transparent and isotropic
5	n-C ₁₁ H ₂₃	0.783 (507) ^e	0.441	0.46	transparent and isotropic
6	n-C ₁₂ H ₂₅	0.690 (506) ^e 0.686 (506) ^f	0.379	0.43	transparent and isotropic
7	n-C ₁₃ H ₂₇	0.571 (505) ^e	0.279	0.41	transparent and isotropic
8	n-C ₁₄ H ₂₉	0.469 (505) ^e	0.200	0.41	transparent but a little anisotropic
9	n-C ₁₅ H ₃₁	0.360 (505) ^e	0.179	0.37	transparent but a little anisotropic

^a See Experimental Section. ^b Reduced to 0.01-mm film thickness. ^c See Table I. Values at λ_{\max} around 500 nm. ^d Determined with crossed polarizers. ^e Values at λ_{\max} indicated in parentheses. ^f Values after 50 cycles of irradiation and subsequent thermal bleaching (70 °C × 10 min).

Table III. Effect of R, R', and A in Vologens Ia,b on Color Development by Light^a

film no.	R	R'	A	abs increase ^b induced by light		isotropic ^c property of film
				ca. 500 nm	610 nm	
10	mixture ^e	H	none	0.612 (507) ^d	0.522 ^f	transparent and isotropic
11	C ₁₂ H ₂₅ ^f	H	none	0.242 (500)	0.793 (613) ^d 0.791 (613) ^h	transparent and isotropic
12	C ₁₂ H ₂₅ ^f	CH ₃	none	0.672 (509) ^d	0.549 (612) ^d	transparent and isotropic
13	C ₁₂ H ₂₅ ^f	H	—CH=CH—	0.322 (535) ^d	0.107 ^f	transparent and isotropic

^a See Experimental Section. ^{b-d} See Table II. ^e Mixture of vologens with R = n-C₈H₁₇, n-C₁₀H₂₁, n-C₁₂H₂₅, and n-C₁₄H₂₉ in an equimolar quantity. ^f Shoulder. ^g 70% n- + 30% highly branched. ^h Values after 50 cycles of irradiation and subsequent thermal bleaching (70 °C × 10 min).

a maximum at C₉₋₁₁ and then become gradually smaller with a further increase in carbon number. The value of the λ_{\max} and the isotropic property of the film determined with crossed polarizers, which is considered to stand for amorphous character, varied corresponding to the photosensitivity change.

It can be concluded from these results that, within the scope of the present experimental conditions, the isotropic property of film Ia is gradually improved with an increase in carbon number to reach the best amorphous character at C₉₋₁₁, causing the highest photosensitivity. The amorphous character becomes worse, however, with a further increase in carbon number, presumably due to the crystallization effect of the long alkyl chains among each other.

It is also known from Table II that better isotropic films may afford larger values of A/A₀, consisting with the results in Table I.

The results summarized in Tables II and III differ from those obtained for vologen crystals, previously reported,^{3a,b} particularly in that this kind of photochromism was observed for all vologen films investigated and associations of radical cations were much more marked especially in the case of R = n-C_nH_{2n+1} (Table II), indicating that the dicationic and counteranionic parts of the vologen molecule are situated next to each other at the sites permitting the general occurrence of the light-induced reaction shown in eq 1 and that the dications tend to lie at the sites, where

the association of the radical cations produced therefrom could take place.

Mixing anions bearing varied R, which may also cause a plasticizing effects, is favorable in that it affords an isotropic film, in which the monomeric radical cation (λ_{\max} , ca. 600 nm) may exist in a high content, and that a high photosensitivity is obtained (see curve 1 in Figure 1 and film nos. 10-12 in Table III).

Vologen Ib bearing the conjugated —CH=CH— group provided similar results. A typical example is given also in Table III (film no. 13).

In this case, however, the absorption peak around 400 nm found for the radical cation from Ia, as seen in Figures 1 and 3, appears to be red-shifted to 535 nm (red coloration) through extended conjugation.

As can be supposed from Tables II and III (expt nos. 6 and 11), vologen films of the present study could be subjected to at least 50 photochromic redox cycles, one of which was composed of the irradiation as described in the Experimental Section and subsequent 10 min standing at 70 °C.

Registry No. 1a (R' = H)(R = n-C₆H₁₃), 136893-34-0; 1a (R' = H)(R = n-C₈H₁₇), 136893-35-1; 1a (R' = H)(R = n-C₉H₁₉), 136893-36-2; 1a (R' = H)(R = n-C₁₀H₂₁), 136893-37-3; 1a (R' = H)(R = n-C₁₁H₂₁), 136893-38-4; 1a (R' = H) (R = n-C₁₃H₂₇), 136893-40-8; 1a (R' = H) (R = n-C₁₄H₂₉), 136893-42-0; 1a (R' = H)(R = n-C₁₅H₃₁), 136893-44-2; 1a (R' = Me)(R = n-C₁₂H₂₅), 136893-45-3; (E)-1b (R' = H)(R = n-C₁₂H₂₅), 136893-47-5.

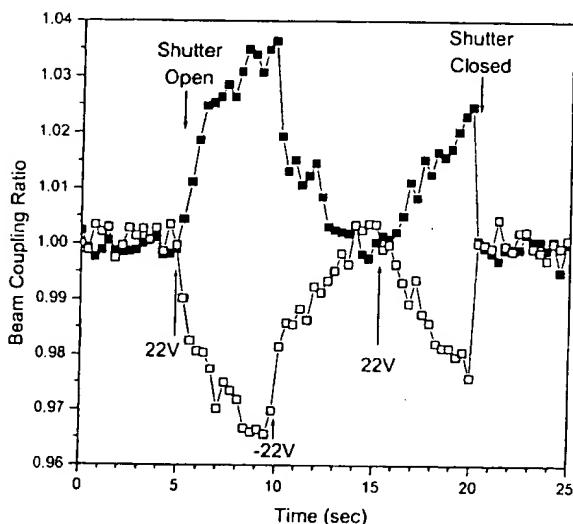


Fig. 4. The change of the beam coupling ratio when the applied voltage is switched from 22 V to -22 V is shown. The rapid initial decrease is due to the reorientation of the FLC director to a less optimal orientation for photorefractivity. The slower change is due to the erasure of the space-charge field.

as charges begin to redistribute in response to the applied field polarity change. At 20 s, the voltage is switched back to 22 V, and the initial charge modulation begins to reform.

We have observed for the first time orientational photorefractivity in FLC composites containing easily oxidized and reduced chromophores. The applied field dependence suggests that the orientational response is a result of the space-charge field coupling to the bulk polarization of the FLC and not to dielectric anisotropy as with nematic liquid crystals. In order to increase the likelihood of observing the linear electronic electro-optic effect in addition to orientational contributions, one possibility is to use homeotropically aligned FLCs with a transverse applied field, so that the modulated space-charge field lies along the polar axis of the FLC. The use of FLCs specifically designed to increase P_S and the electronic electro-optic effect would also prove advantageous for improving the performance of these novel materials.

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Flexible Smart Window via Surface Graft Copolymerization of Viologen on Polyethylene

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The development of chromogenic materials for glazing "smart" or "intelligent" windows has been actively pursued in recent years. The change in the optical properties of these materials may be activated by electricity, heat, or light. Examples of commonly used chromogenic materials are certain transition-metal oxides such as WO_3 , NiO , MoO_3 , and organic compounds such as viologens, diphthalocyanines, and polyaniline.^[1-5] The viologens are among the most studied chromogenic materials and the change in coloration is achieved by an oxidation-reduction reaction. However, since the short-chain viologens are soluble in water, various methods of synthesizing viologen-containing chromogenic systems have been developed. These include the incorporation of viologens into anionic polyelectrolyte films,^[6] iminodiacetic acid-type chelate resin beads,^[7] and *N*-vinyl-2-pyrrolidone-methyl acrylate copolymers,^[8] as well as the casting of ruthenium(II) complex and viologen containing partially quaternized poly(1-vinylimidazole) into films.^[9]

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Our group and others have carried out surface modification of polymeric substrates via graft copolymerization to impart new and specific functionalities to the polymer surface.^[10-14] In this paper, we report on the use of this strategy to incorporate a thin layer of viologen polymer on the surface of low-density polyethylene (LDPE) film. This viologen-LDPE system serves as a transparent "smart" window whose transmittance is reduced when exposed to light. This type of system offers the advantage of being a thin flexible film that can be shaped and is suitable for large area displays. Furthermore, the thin surface layer of viologen polymer offers a rapid photochromic response.

The method we employed to covalently bond the viologen moieties onto the surface of the LDPE film involves first the UV-induced graft copolymerization of 4-vinyl benzyl chloride on the plasma-pretreated LDPE film surface. The pendent benzyl chloride groups of the grafted 4-vinyl benzyl chloride polymer chain on LDPE film surface then serve as functional groups for the introduction of the viologen moiety onto the LDPE surface via reaction with 4,4'-bipyridine followed by benzyl chloride or other alkyl halides. The reaction route is given in Scheme 1. The proportion of the 4-vinyl benzyl chloride successfully reacted with 4,4'-bipyridine is represented by "y" in Scheme 1. The amount of viologen on the film surface can be varied by varying the amount of vinyl benzyl chloride grafted on the film surface (Step 1 in Scheme 1) and the type of alkyl halides (e.g., benzyl chloride) used in the subsequent reaction (Step 3 in Scheme 1). The graft concentration of the vinyl benzyl chloride in turn depends on the monomer concentration, the plasma treatment time, and the UV-induced reaction time. Table 1 shows how the plasma treatment time

Table 1. Surface graft concentration of 4-VBzCl copolymer as a function of argon plasma treatment time and UV-induced reaction time.

Sample no.	Argon plasma treatment time [s]	UV-induced reaction time [min]	Graft concentration [a]
1	60	15	0.14
2	60	20	0.22
3	60	30	0.40
4	60	60	0.48
5	60	120	0.27
6	90	15	0.05
7	90	20	0.05
8	90	30	0.06
9	90	45	0.24
10	90	60	0.44
11	90	120	0.19

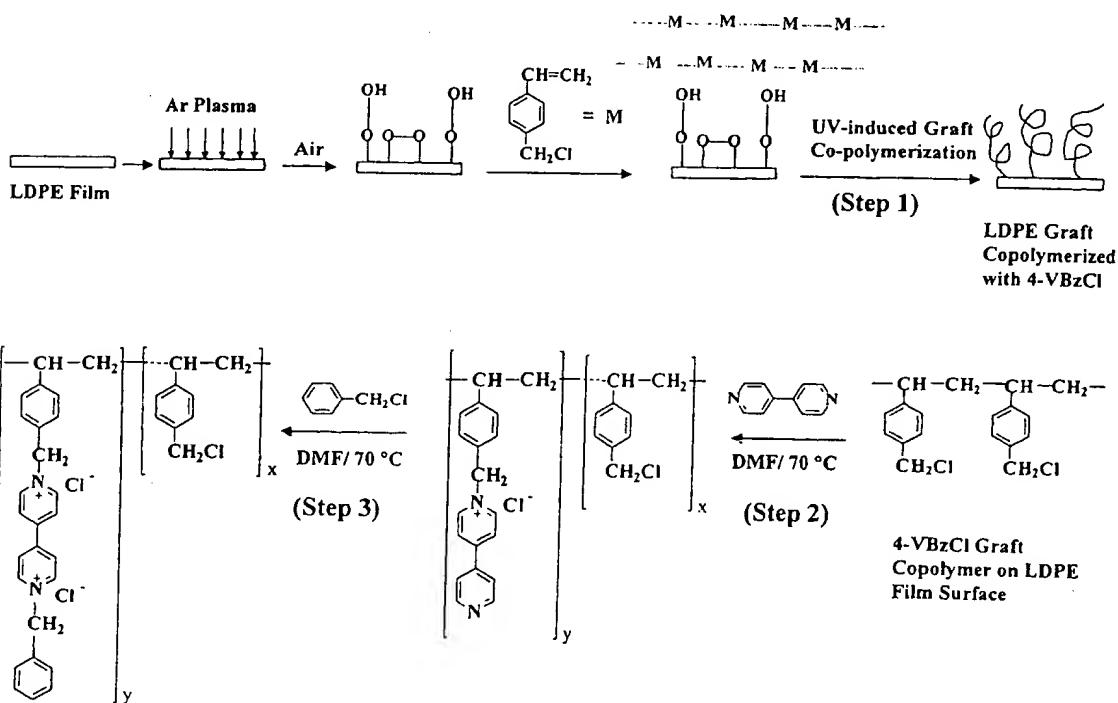
[a] Obtained from XPS measurement using the following equation:

$$\frac{M_{VBzCl}}{M_{ethylene}} = \frac{\text{peak area of Cl 2p}}{[\{\text{peak area of total C 1s}\} - \{(\text{peak area of Cl 2p}) \times 9\}]/2} \quad (1)$$

where the peak area has been corrected with the appropriate sensitivity factor, and the factors of 9 and 2 account for the nine carbon atoms associated with each 4-VBzCl unit and the two carbons per repeating ethylene unit, respectively.

and the UV-irradiation time affect the graft concentration of vinyl benzyl chloride (defined as number of vinyl benzyl chloride units per repeating ethylene unit of LDPE).

The viologen grafted LDPE films were characterized by UV-vis absorption spectroscopy and X-ray photoelectron spectroscopy (XPS) measurements. The UV-vis absorption spectrum of the film (labeled "before irradiation" in Fig. 1) shows an absorption band below 380 nm attributable to the viologen dication (denoted as BV^{2+} for benzyl viologen).^[15] During the XPS measurements, the color of the film in the XPS chamber was observed to change from very faint yellow to blue. The color change is due to the reduction of the BV^{2+}



Scheme 1. Reaction route used to synthesize the viologen grafted LDPE films.

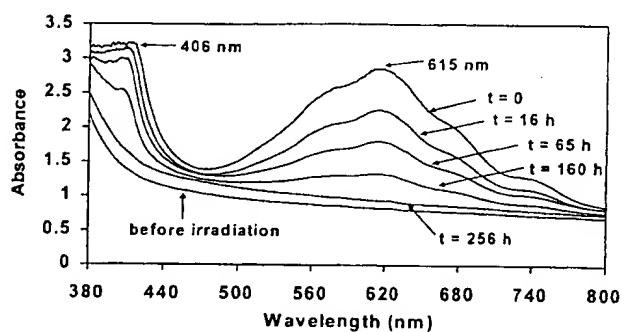


Fig. 1. UV-vis absorption spectra of viologen grafted LDPE film before and after 3 min irradiation and during bleaching under vacuum. (Time indicated denotes the time after irradiation has stopped.)

to the monocation radicals (BV^{+*}) under X-ray irradiation and has also been reported earlier.^[16] The XPS N 1s core level spectrum of the viologen grafted LDPE film shows two well resolved peaks due to nitrogen radical (N^*) at 399.6 eV and positively charged nitrogen (N^+) at 401.8 eV (as illustrated in Figure 2a for Sample 10). There is no peak due to the neutral nitrogen atom ($-N=$), which suggests that Step 3 is efficient at

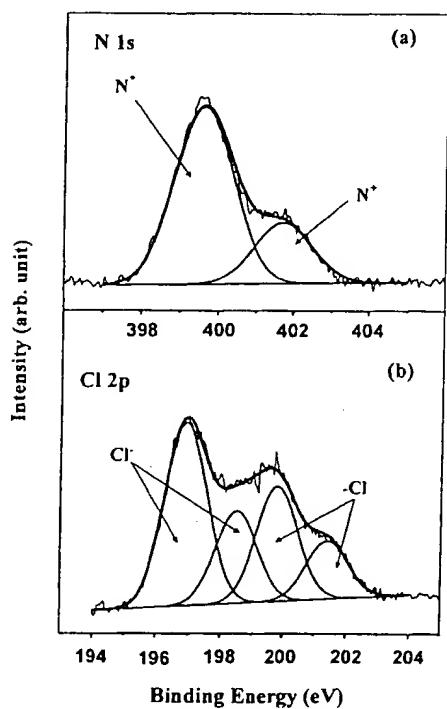
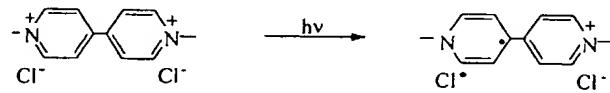


Fig. 2. XPS a) N 1s and b) Cl 2p core level spectra of a viologen grafted LDPE film (Sample 10).

converting both N atoms of the bipyridyl ring to the diquaternized nitrogen cation (N^+). The Cl 2p core level spectrum shows component peaks due to chloride anions, Cl^- , and covalently bonded chloride, $-Cl$ (Fig. 2b). The presence of the latter indicates that some benzyl chloride groups in the 4-vinyl benzyl chloride graft copolymer did not react with the 4,4'-bipyridine (proportion represented by "x" in Scheme 1). This may be due to steric hindrance between the benzyl rings, which inhibits the reaction of the 4,4'-bipyridine with every

benzyl chloride group. The Cl^-/N^+ ratio of the viologen grafted films is readily calculated from the deconvoluted XPS N 1s and Cl 2p spectra. The Cl^-/N^+ ratio calculated for the viologen grafted LDPE films with vinyl benzyl chloride graft concentration ranging from 0.05 to 0.44 is between 0.82 and 1.04. This confirms that charge neutrality is maintained. Hence, the UV-vis absorption spectroscopy and XPS measurements confirm the presence of viologen moieties that are covalently bonded to the LDPE surface even after extensive washing with organic solvents (please refer to the Experimental section).

A number of applications can be envisaged for polymeric substrates with surface graft copolymerized viologen moieties. When the viologen grafted LDPE films are exposed to near-UV irradiation for 1 to 3 min at room temperature, the color of the film changes from faint yellow to blue. As mentioned earlier, this color change results from the conversion of the viologen dications to the monocations^[15] and may be represented by Scheme 2.^[8,17]



Scheme 2. Photoinduced conversion of viologen dication to monocation.

When the irradiation is stopped, the reverse reaction $BV^{+*} \rightarrow BV^{2+}$ occurs. These color changes occur very rapidly in air. To illustrate these color changes, experiments to record the UV-vis absorption spectra of the film were carried out with the film in a vacuum tube. Figure 1 shows the UV-vis spectrum of the Sample 3 film immediately after irradiation by a high-pressure 1 kW Hg lamp placed 4 cm from the film ($t = 0$ curve) and the spectra as the film bleaches with time under vacuum. The shape and position of absorption maximum (λ_{max}) of the $t = 0$ curve is quite similar to those reported earlier for radical cations derived from the viologens in solution,^[18] or in the form of crystals^[19] or films.^[17,20] The viologen monocation radical (BV^{+*}), which is the one-electron reduced form of viologen dication, gives rise to λ_{max} at about 615 nm and 406 nm, while that of its associated species or the dimeric form (BV_2^{2+}) is at about 560 nm.^[15,17,21] The response of the viologen grafted film to several cycles of irradiation and bleaching is shown in Figure 3. These experiments were carried out with a filter, which reduces the intensity of the 1 kW Hg lamp by 50 % and cuts off the irradiation below 350 nm. From Figure 3, it can be seen that the response of the film is very rapid in air (compared to Fig. 1, which shows the slow bleaching in vacuum). This film exhibits a high degree of stability and after 8 cycles, the maximum absorbance at 615 nm does not change significantly (<1%). The response time curve during bleaching also remains essentially unchanged.

In conclusion, we have demonstrated a technique whereby a thin layer of viologen can be incorporated via surface graft copolymerization with a polymeric substrate. The latter lends mechanical strength and flexibility while the thin viologen layer minimizes the amount of viologen required and offers a rapid and reproducible response to UV-vis irradiation. Work

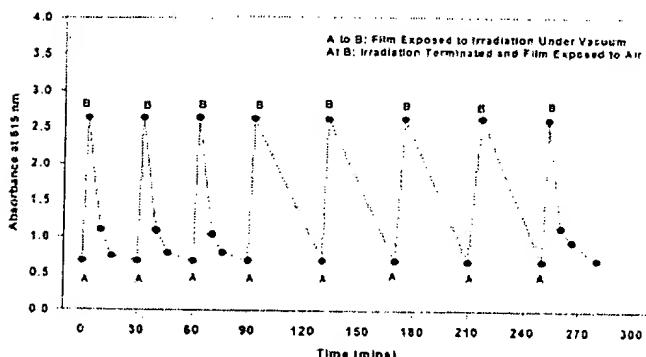


Fig. 3. Response of viologen grafted LDPE film (Sample 3) subjected to cyclic irradiation. (For cycles 1-3 and 8, the absorbance at 615 nm was monitored 7, 13, and 30 min after termination of irradiation. For cycles 4-7, the absorbance was measured 40 min after termination of irradiation.)

is in progress on extending this technique to complexes of viologen with other chromogenic materials and on tailoring these complexes to specific applications.

Experimental

Materials and Reagents: 4-vinyl benzyl chloride (4-VBzCl) (monomer) used for graft copolymerization was obtained from Sigma Aldrich at a purity of 90% (other isomers account for the remaining 10%) and was used as received. Benzyl chloride was obtained from BDH (purity 98.5%) and used without further purification. 4,4'-Bipyridine was obtained from Sigma Aldrich and used as received. The solvents and other reagents were of reagent grade and were used without further purification. LDPE film (of thickness 0.125 mm) was obtained from Goodfellow Corporation, UK.

Material Characterization: The UV-vis absorption spectra were recorded on a Shimadzu Model UV-3101PC. The XPS measurements were made on an AXIS HSi-165 ULTRA spectrometer (Kratos Analytical Ltd, England) with a Mg K α X-ray source (1253.6 eV photons). The details of the experiment are given in previous publications [13,22].

Viologen Grafting on LDPE Film: LDPE films were cut into 2 cm \times 5 cm pieces, washed with acetone (using an ultrasonic bath for 1 h), and then dried under vacuum for 1 h. The cleaned LDPE films were treated with Ar plasma for either 60 s or 90 s on each side in an Anatech SP100 plasma system, equipped with a cylindrical quartz reactor chamber. The glow discharge was produced at a plasma power of 35 W, an applied frequency of 40 kHz, and an argon pressure of 0.6 torr. The plasma-treated films were exposed to the atmosphere for about 5 min to facilitate the formation of surface peroxides and hydroperoxides, which would initiate the subsequent graft copolymerization of 4-vinyl benzyl chloride monomer. A drop of 4-vinyl benzyl chloride (approximately 50 μ L) was spread on both sides of the Ar plasma-pre-treated film, which was then tightly clipped between two quartz plates and placed in a UV photochemical reactor (Riko Rotary, Model RH 400-10W) for a predetermined period of time (from 10 min to 2 h) at 25°C. After UV irradiation, the film was removed from the plates (after a few hours of soaking in ethanol or DMF solution).

The LDPE film after reaction with vinyl benzyl chloride was washed with dimethylformamide (DMF) for a few hours to remove the residual monomer and homopolymer from the film. After washing, the film was dried under vacuum for 2 h before reacting with 10% w/v 4,4'-bipyridine in DMF solution (30 mL). The reaction mixture was heated in a water bath at 70°C for 10 h. The films were then removed from the solution, washed with DMF and acetone, and further treated with benzyl chloride in DMF (30 mL) for another 10 h at 70°C. The films were taken out, washed thoroughly with DMF and ethanol, and then dried under vacuum for 1 h. Since the viologen grafted films are sensitive to light, these films were stored in the dark before they were subjected to further testing.

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Electron Transport in Fluorinated Copper-Phthalocyanine

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Transistor circuits based on organic transistors have been proposed for a variety of applications such as large-area electro-optic displays or identification tags.^[1-3] For digital circuits the advantages of complementary logic include low power dissipation, robust operation, and ease of circuit design. However, only a few organic semiconductors have proven high performance and stability in air for n-channel operation.^[4-6] One of these promising materials is copper hexadecafluorophthalocyanine ($F_{16}CuPc$). Thin-film field-effect transistors (FETs) with mobilities exceeding 10^2 cm 2 /Vs have been demonstrated.^[4] In addition, large-scale integration and fast complementary logic circuits have been reported.^[7,8] In order to improve device performance and understand the intrinsic charge transport mechanism, we studied the electrical properties of $F_{16}CuPc$ single crystals in air as functions of time and temperature. Furthermore, we investigated the mobility in thin-film devices as functions of gate bias and temperature.

Single crystals of $F_{16}CuPc$ have been grown from the vapor phase in a stream of gas using a similar technique as for other organic semiconductor materials.^[9] Needle-like single crystals of several mm length and several 100 μ m width were obtained. The charge-transport properties in the direction parallel to the long axis (*b*-axis) of the samples with thermally evaporated

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